ABSTRACT

Kelkar, Aniruddha V. Ph.D., Purdue University, September 2014. On The Theory of Brownian Aggregation in Colloidal Dispersions. Major Professors: Elias I. Franses and David S. Corti.

Brownian aggregation kinetics is a topic of interest for colloidal dispersions, macromolecular fluids, nanoparticle self-assembly, and biochemical reactions. The manipulation of colloidal dispersion stability by containing or promoting aggregation rates is manifest in several natural phenomena and engineering applications. The destabilization of silt dispersions as river water mixes with the high-ionic-strength seawater near river system deltas leads to the deposition of fertile soil on the river banks. Pigments used in the stone age paintings found in the Lascaux caves of France and in the written records of Egyptian pharaohs are early examples of stabilized colloidal dispersions. Present day applications include the manufacturing of paints and coatings, inkjet printing, formulation of food and pharmaceutical dispersions, waste-water treatment, and in the transport of solids during oil production. Aspects of this problem are also important in biological systems and affect cellular organization, enzyme catalysis, protein aggregation, and macromolecular binding. The primary focus of the thesis is on the fundamental study of this problem.

Brownian aggregation in concentrated dispersions of hard spheres, interacting spheres — van der Waals or DLVO potential, and binary mixtures of hard spheres is examined. Much of the current understanding of Brownian aggregation kinetics stems from the models of Smoluchowski and Fuchs. These classical approaches are evaluated using a more rigorous coarse-grained technique — Brownian dynamics simulation. The predictions of these two models agree with simulation results only for

very dilute dispersions, $\phi < 0.005$, with errors of up to three orders of magnitude in more concentrated systems. For most applications, these classical models are thus inadequate. Using approaches from within the "liquid-state" dynamic density functional theory, new models for Brownian aggregation are developed. The predictions of the new models are in excellent agreement with the simulation results. On the basis of these models, a new mechanistic understanding for Brownian aggregation in concentrated dispersions is gained: the higher aggregation rates result from short-range ordering, non-idealities in particle diffusion, and unsteady-state effects. Moreover, explanations for rate constant asymmetry and time lag in aggregation kinetics are provided for the first time.

Furthermore, some more applied but related problems are also studied. A simple model is developed to account for the effect of aggregation on the sedimentation dynamics of colloidal dispersions. Aspects of the phase behavior and stability in certain model water in oil emulsions are also investigated. Finally, a population balance framework is developed to account for the effects for aggregation on the transport of solids in oil production.